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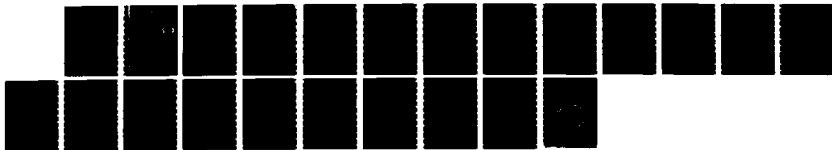
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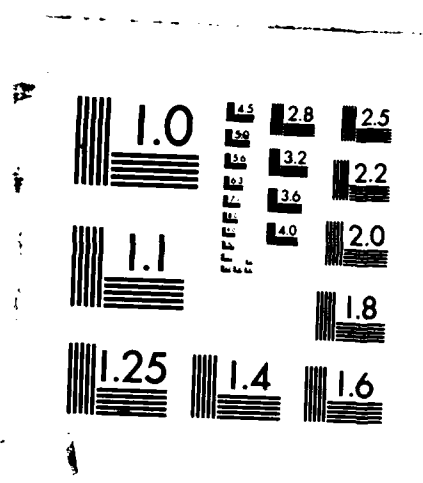
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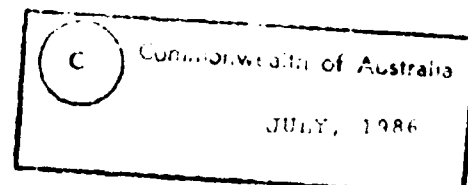
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BENZOTRIAZOLES AS ENERGETIC MATERIALS

A.M. Pitt and W.S. Wilson

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Adrian M. Pitt and William S. Wilson

ABSTRACT

Treatment of 2-aminodiphenylamines with nitric acid or nitrous acid has yielded nitro-substituted 1-phenylbenzotriazoles. These materials have been examined as potential energetic materials, with particular reference to their densities, thermal properties, sensitiveness characteristics and explosive properties.



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ABSTRACT

Treatment of 2-aminodiphenylamines with nitric acid or nitrous acid has yielded nitro-substituted 1-phenylbenzotriazoles. These materials have been examined as potential energetic materials, with particular reference to their densities, thermal properties, sensitiveness characteristics and explosive properties.

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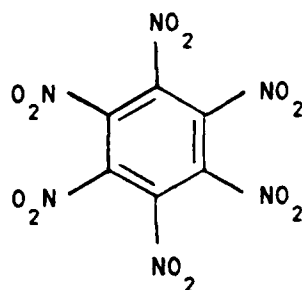
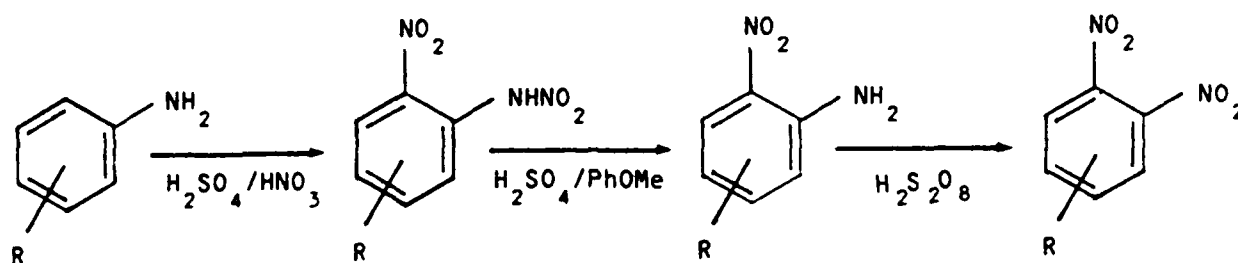
BENZOTRIAZOLES AS ENERGETIC MATERIALS

1. INTRODUCTION

Polynitrodiphenylamines are sought as new dense energetic materials, and for structure/property correlations, as part of an explosives synthesis programme. Derivatives substituted with not more than three nitro groups in one aromatic ring are readily prepared by direct nitration and/or coupling reactions. However, more highly nitrated compounds are not accessible by these routes, due to the deactivating effect of nitro substituents and the lability of nitro groups flanked by two adjacent nitro groups.

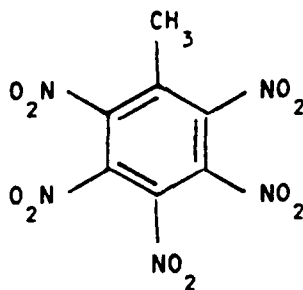
The stratagem which has been used to synthesise highly nitrated aromatics involves mixed acid nitration of a suitable nitroaniline, often prepared by selective reduction of a polynitroaromatic, cleavage of the nitramine using sulphuric acid in anisole to produce a polynitroaniline which is finally oxidised using peroxydisulphuric acid (scheme 1). Compounds prepared by this route include hexanitrobenzene (HNB) (1) [1], pentanitrotoluene (PNT) (2) [2] and decanitrobiphenyl (DNBP) (3) [3]. This method was extended to the synthesis of other highly nitrated polynitroaromatics, and to investigate similar reactions using diphenylamines. However, attempts at nitration of these diphenylamines led unexpectedly to benzotriazoles. This report describes the synthesis of several of these compounds and a preliminary examination of their explosive properties.

Scheme 1



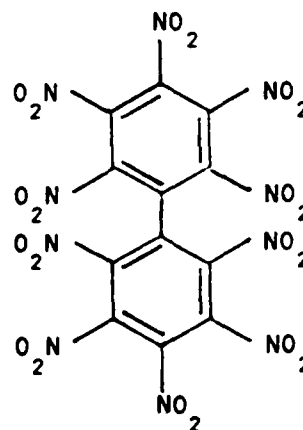
HNB

(1)



PNT

(2)



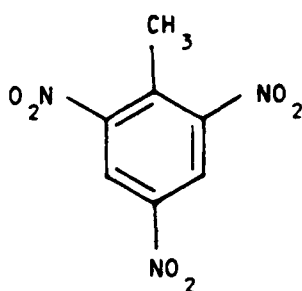
DNBP

(3)

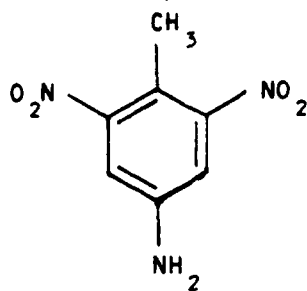
2. RESULTS AND DISCUSSION

2.1 Synthesis of Materials

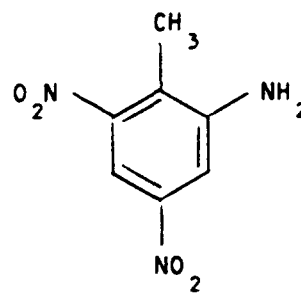
2,4,6-Trinitrotoluene (TNT) (4) can be selectively reduced with hydrogen sulphide in dioxan to give 4-amino-2,6-dinitrotoluene (5) [4] or by using iron powder in acetic acid to give 2-amino-4,6-dinitrotoluene (6) [2]. Hydrogen sulphide reduction of 2,4,6-trinitrodiphenylamine (7), chosen as a model compound to develop the procedure and prepared conveniently by the reaction of aniline with picryl chloride [5], failed to yield a recoverable product but reduction using iron powder in acetic acid [6] gave 2-amino-4,6-dinitrodiphenylamine (8) in good yield.



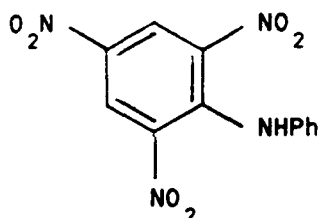
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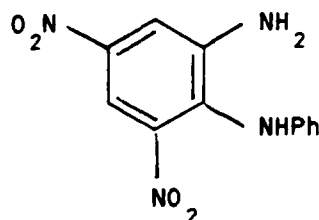
(5)



(6)

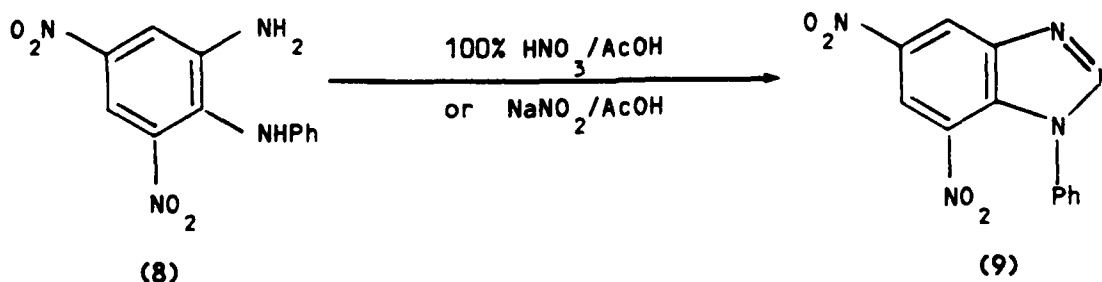


(7)



(8)

Mixed acid nitration of (8) gave only highly coloured solutions from which no product could be isolated. However dissolution of (8) in acetic acid followed by treatment with 100% nitric acid gave a yellow solid, which was shown spectroscopically not to possess any amino groups. The ^1H n.m.r. spectrum in d_6 -DMSO displayed only two meta coupled doublets, each one proton, at δ 9.51 and 9.07 ($J \sim 2$ Hz) and a five proton singlet at δ 7.61. The same material was also obtained on treatment of an acetic acid solution of (8) with sodium nitrite, and the compound was identified as 1-phenyl-5,7-dinitrobenzotriazole (9).

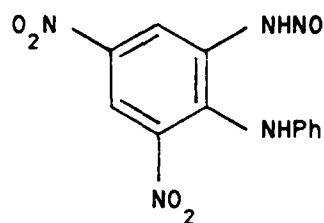


(8)

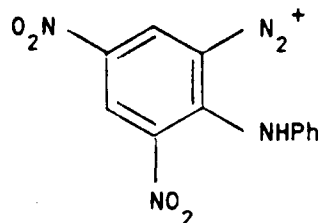
(9)

The formation of (9) by treatment of (8) with sodium nitrite is readily understood in terms of dehydration of an intermediate nitrosamine (10), or cyclisation of the diazonium cation (11) followed by deprotonation. Formation of (9) by action of nitric acid on (8) might result from reaction of oxides of nitrogen present in the nitric acid, or by deoxygenation of the

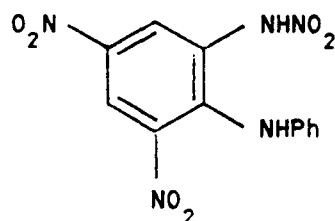
2-N-oxide (13) formed conceptually by dehydration of the nitramine (12). It should be noted that while benzotriazole-1-oxides [7] have been described benzotriazole-2-oxides appear to be unknown.



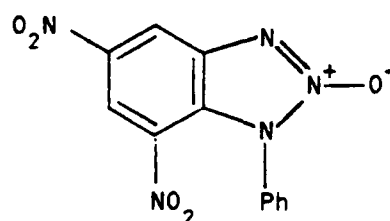
(10)



(11)

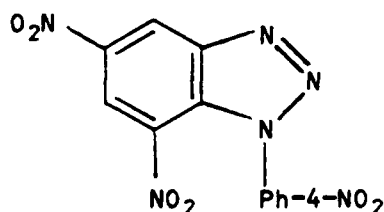


(12)



(13)

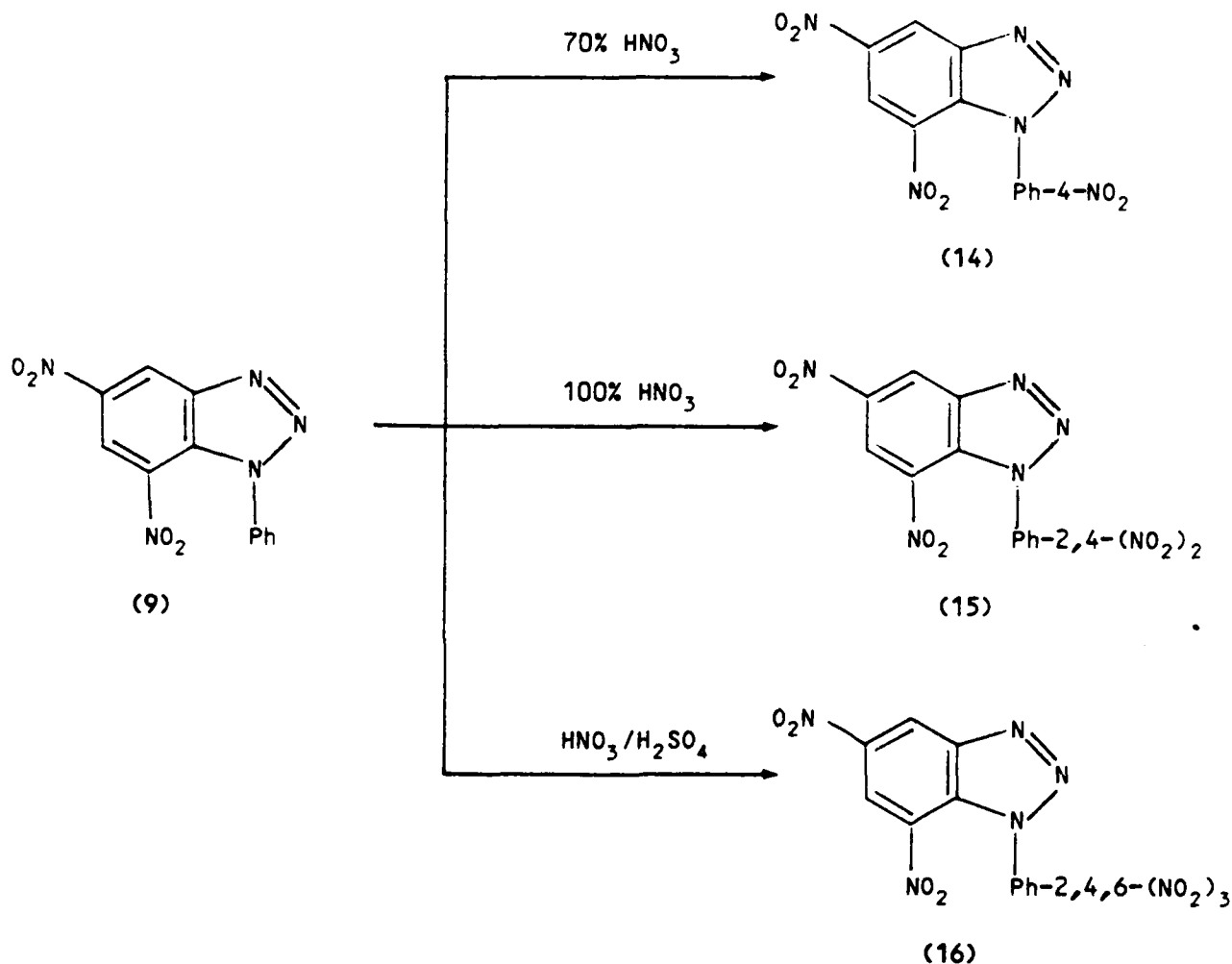
Treatment of (8) with hot 54% nitric acid gave a 1:2 mixture of (9) and 1-(4'-nitrophenyl)-5,7-dinitrobenzotriazole (14). A mixture of the same products was also obtained on treatment of (8) with nitronium tetrafluoroborate in sulpholane, either at ambient temperature or at 110°C. These latter conditions are less likely to favour the presence of oxides of nitrogen, perhaps giving greater support to the intermediacy of such species as (12) and (13).



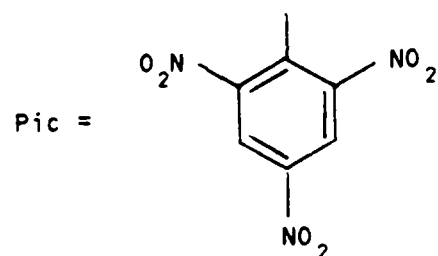
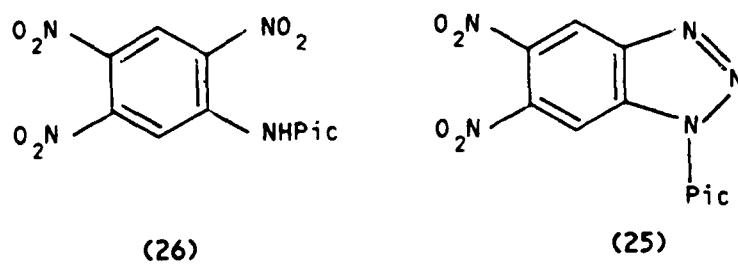
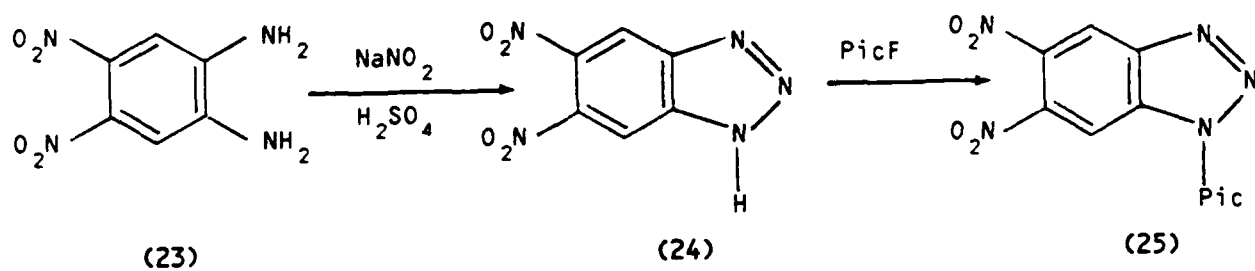
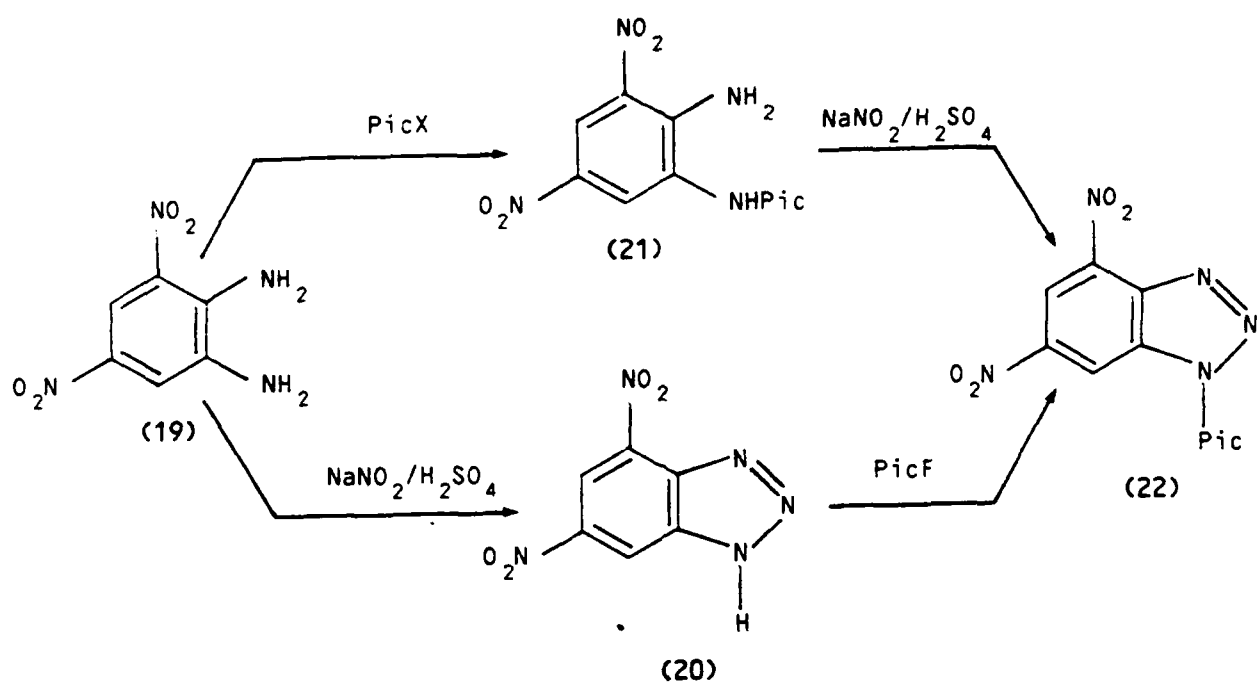
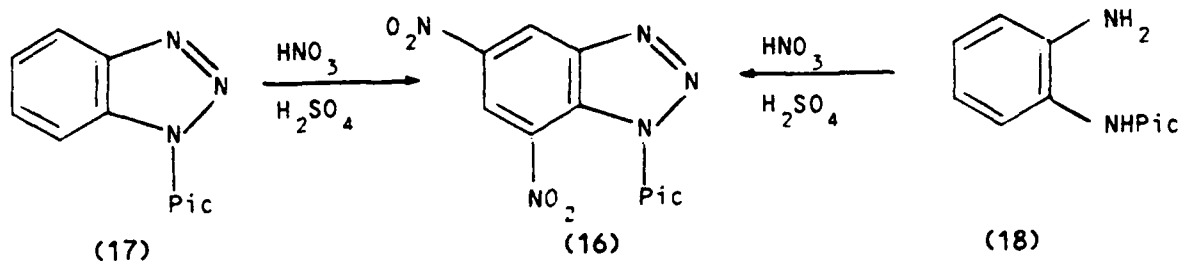
(14)

Dissolution of (9) in 54% nitric acid and heating under reflux failed to give the expected nitration to (14), and the starting material was reclaimed in quantitative yield. This suggests that the formation of (14) on nitration of (8) resulted from competitive nitration of the phenyl ring in (8) followed by cyclisation. However more vigorous reaction conditions led to smooth and selective nitration of (9) in excellent yield. Nitration in 70% nitric acid under reflux gave (14), nitration using 100% nitric acid gave 1-(2',4'-dinitrophenyl)-5,7-dinitrobenzotriazole (15), while mixed acid

nitration gave 1-(2',4',6'-trinitrophenyl)-5,7-dinitrobenzotriazole (16). In each case the structure was assigned on the basis of i.r. (no NH absorption) and ^1H n.m.r. spectra (presented in Table 1). While different nitrating mechanisms are suggested (by product characterisation) for 100% HNO_3 in AcOH and hot 54% HNO_3 , investigations as to the nitrating species present were beyond the scope of this study.



Coburn prepared (16) [8] (which he named BTX and proposed as a thermally stable explosive suitable for use in exploding bridgewire detonators [9]) by mixed acid nitration of the benzotriazole (17). We obtained the same product on mixed acid nitration of the amine (18). Among other compounds, Coburn also prepared the isomers (22) and (25) from 3,5- and 4,5-dinitro-o-phenylenediamine (19) and (23) respectively [8]. We have now prepared (22) via the amine (21), and (25) by the action of sodium nitrite on an acetic acid suspension of (26). The structures of (22) and (25) followed from i.r. and ^1H n.m.r. spectra (given in Table 1).



2.2 Assessment of Explosive Performance

2.2.1. Density

The densities of the benzotriazoles (9), (14), (15), (16), (17), (22) and (25) were measured using a gas comparison pycnometer and are presented in Table 2 together with the values estimated using Stine's procedure [10]. The latter is a simple empirical group additivity method which does not differentiate between isomers, nor does it take into consideration molecular shapes and steric interactions. Thus while the density measured for (9) is in excellent agreement with the calculated value, the more highly nitrated materials (15) and (16) are somewhat less dense than predicted. These lower densities presumably result from reduced coplanarity of the phenyl and benzotriazole ring systems arising from steric interaction between the proximate nitro substituents at the 2'- and 6'- and 7-positions respectively. There are no such interactions in (17) and (22) and the observed densities are very close to the predicted values. Additionally interaction between the adjacent nitro groups of (25) force them out of the plane of the benzotriazole ring, and the density is lower than expected.

2.2.2. Thermal Properties

The benzotriazoles (9), (14), (15), (16), (17) and (25) all melted sharply, with no sign of decomposition, at temperatures between 150° and 260°. The benzotriazole (22) did not melt below 260°.

The thermal analysis results obtained by DSC are shown in Table 3. Except, in the case of (22), the first event observed was melting, with no sign of decomposition, with the fusion endotherm in the range 6-10 kcal mole⁻¹. Although the phenyl compound (9) showed no sign of exothermic reaction, compounds (14), (15) and (16) exhibited an exotherm following the fusion endotherm. The magnitude of the exotherm increased, as might be expected, with the degree of nitration. These results suggest that while certainly (16) and probably (15) may be sufficiently energetic to be useful as explosives, compounds (9) and possibly (14) are unlikely to be satisfactory. The isomeric (25) also showed a melting endotherm and a large exotherm, while (22) showed no sign of melting and a slightly smaller exotherm. Interestingly, 1-picryl benzotriazole (17) showed a much larger exotherm than either (14) or (15), suggesting that the picryl group contributes more energy to the molecule than does the dinitrobenzotriazole moiety.

The benzotriazoles were also examined using the ERDE temperature of ignition test, in which 50 mg unconfined samples are heated at 5°C min⁻¹ in a test tube. The temperature of ignition is that at which the sample ignites or (more usually) explodes [11]. While the picryl derivatives (16), (17), (22) and (25) ignited to explosion during this test, the others simply sublimed and charred.

2.2.3. Explosive Properties

The velocity of detonation and detonation pressure for each of the benzotriazoles (Table 4) were estimated using the empirical method of Rothstein and Peterson [12]. This simple method has the advantage that the detonation parameters are derived solely from molecular formulae and

structures, and requires no knowledge of physical, chemical or thermochemical properties. It is consequently unable to distinguish between isomers.

The impact sensitivity of the benzotriazoles (9), (14), (15) and (16) was measured using the Rotter Impact Test, which monitors the response of 30 milligrams of explosive placed in a metal cup to the impact of a 5 kg weight dropped onto it. A Figure of Insensitiveness (F of I) is obtained by comparison of the 50% "explosion" height for the material with that for a standard grade of RDX to which is assigned an F of I of 80 [11]. The impact sensitivity of (22) was also measured, and although insufficient of (17) and (25) was available for complete testing, "screening" tests were carried out on these materials. Results are presented in Table 4.

The electrostatic spark sensitivity of the benzotriazoles (9), (14), (15) and (16) was measured using the ERDE electric spark test, in which the loose powder is subjected to discharges of 4.5, 0.45 and 0.045 joules energy [11]. The results are also given in Table 4.

The expected increase in the explosive output of the benzotriazoles with the degree of nitration is again reflected in the calculated velocity of detonation and detonation pressure. The values in Table 4 would once more suggest that while the picryl derivatives (16), (22) and (25) and probably the 2,4-dinitrophenyl compound (15) are sufficiently energetic to be useful explosives the less nitrated (9), and possibly (14) and (17), are not.

The increase in predicted explosive output with the degree of nitration is paralleled by an increase in the sensitivity to impact of the benzotriazoles (9), (14), (15) and (16). Thus 1-phenyl-5,7-dinitrobenzotriazole (9) is virtually insensitive to impact, (14) and (15) are progressively more sensitive, whereas 1-picryl-5,7-dinitrobenzotriazole (16) shows impact sensitivity typical of intermediate or primary explosives. The 4,6-dinitro isomer (22) shows similar sensitivity, and limited screening tests indicate that the 5,6-dinitro isomer (25) and 1-picrylbenzotriazole (17) do also. It is apparent that the picryl group contributes more to impact sensitivity than does nitration in the benzotriazole ring, and it is probable that the "trigger linkage" [13] for impact initiation is associated with the picryl group. The relatively minor variation in sensitivity between the isomeric compounds (16), (22) and (25) may be accounted for in terms of steric interaction between the 7-nitro group and the picryl function in (16) and between the adjacent 5- and 6-nitro groups in (25).

There is also an increase in the electrostatic sensitivity of the benzotriazoles (9), (14), (15) and (16) with the degree of nitration, but none of these compounds would be regarded as particularly sensitive to this stimulus.

3. CONCLUSION

Variously nitrated 1-phenylbenzotriazoles have been examined as potential energetic materials, with reference to their densities, thermal properties, sensitiveness characteristics and explosive properties. Densities and calculated explosive properties (velocity of detonation and detonation

pressure) increase with the degree of nitration, as does the energy released on thermal decomposition and sensitiveness to impact. In the case of the latter two properties, however, it is also clear that nitration of the phenyl substituent to produce a picryl derivative has more effect than does nitration in the benzotriazole ring, and it appears that the picryl group provides the "trigger linkage" for impact initiation.

4. EXPERIMENTAL

Warning! Many of the polynitro compounds described herein are potentially powerful and sensitive explosives, and should be handled appropriately.

¹H n.m.r. spectra were recorded using a Varian EM360L nmr spectrometer on solutions in d₆-dimethylsulphoxide containing tetramethylsilane as internal standard; data for most compounds is listed in Table 1. Infrared spectra were obtained using a Perkin Elmer 683 spectrophotometer using potassium bromide discs. Melting points were measured using a Reichert Heizbank hot strip and are corrected.

Densities were measured using a gas comparison pycnometer (Systems Science and Software Type G 102-28). Each compound was subjected to thermal analysis using a Perkin Elmer DSC-2 Differential Scanning Calorimeter fitted with a Scanning Auto-Zero accessory and a Thermal Analysis Data Station. All samples (0.40 - 1.00 mg) were weighed accurately on a Mettler ME30 analytical balance directly into aluminium sample pans, and lids were placed (not crimped) over the samples. The sample and reference compartments of the calorimeter were purged continuously with nitrogen gas at 20-25 mL min⁻¹ throughout the DSC scans, which were carried out at a heating rate of 20 K min⁻¹ over a temperature range 330 - 800 K. The output was calibrated using samples of indium (m.p. 429.8 K), tin (m.p. 505.1 K), lead (m.p. 600.7 K) and zinc (m.p. 692.7 K).

2,4,6-Trinitrodiphenylamine (7).

This compound was prepared as an orange solid (72%) m.p. 180° (lit. m.p. 179-80°) by the method of Davis and Ashdown [5].

2-Amino-4,6-dinitrodiphenylamine (8).

Iron powder (4 x 0.41 g) was added to a stirred solution of the amine (7) (4.0 g) in acetic acid (100 mL) under dry nitrogen at 30 min intervals. After 2.5 h the mixture was filtered, the filtrate was poured into water (1.2 L) and the resulting precipitate was collected, dried and recrystallised from ethanol. 2-Amino-4,6-dinitrodiphenylamine (2.57 g; 71%), was obtained as red-orange needles m.p. 160-1° v_{max}: 3460, 3370, 3340, 1580, 1540, 1500, 1350, 1320, 1295 and 1340 cm⁻¹; ¹H n.m.r.: δ 8.25, 1H, s, NH; 7.82, 2H, AB quartet, H₃, H₅; 7.4-6.6, 5H, m, Ph; 8.90, 2H, s, NH₂.

Nitration of 2-amino-4,6-dinitrodiphenylamine (8)

The diamine (8) (0.5 g) was suspended in acetic acid (20 mL) and nitric acid (100%, 2 mL) was added dropwise over 10 mins with stirring. Filtration after a further 5 mins gave a yellow solid (0.3 g) and pouring of the mother liquor into water (120 mL) gave a further, brown solid (0.2 g). The bulk products were chromatographed (silica/methylene chloride) to give a yellow solid (0.47 g) which on recrystallising from ethanol afforded 1-phenyl-5,7-dinitrobenzotriazole (9) (0.44 g, 83%) m.p. 208°. ν_{\max} : 3080, 3040; 1580, 1530, 1330 cm^{-1} . The same product was also prepared, in similar yield, by addition of sodium nitrite to a suspension of the diamine (8) (0.50 g) in acetic acid (20 mL).

The diamine (8) (0.5 g) was dissolved in 54% nitric acid (20 mL) and heated overnight under reflux. Pouring into water (100 mL) gave a yellow solid (0.46 g) which was shown by chromatography and ^1H n.m.r. spectra to be a mixture. Chromatography (silica/methylene chloride) gave (9) (0.15 g) and a second solid (0.3 g; 51%) which recrystallised from ethanol as an off white solid, m.p. 204°, identified as 1-(4'-nitrophenyl)-5,7-dinitrobenzotriazole (14). ν_{\max} : 3080, 1590, 1530, 1340 cm^{-1} .

The diamine (8) (0.5 g) was added to a suspension of nitronium tetrafluoroborate (0.2 g) in sulpholane (10 mL) and stirred at room temperature for 2 h. Quenching in ice/water (200 mL) and trituration followed by filtration gave a brown solid. Chromatography (silica/methylene chloride) gave (9) (0.22 g) and (14) (0.11 g), identical with the materials prepared above. Carrying out the reaction for 24 h at 110° gave the same products in the ratio 1:1.

Nitration of 1-phenyl-5,7-dinitrobenzotriazole (9)

The benzotriazole (9) (0.5 g) was heated in nitric acid (70%, 20 mL) at 80° for 36 h. Quenching in ice/water (200 mL) gave a white solid which was recrystallised from ethanol to give (14) (0.40 g; 69%), m.p. 204°.

The benzotriazole (9) (0.5 g) in acid (100%, 20 mL) and heated at 80° for 24 h. Quenching in ice/water (200 mL) gave a very pale yellow solid (0.55 g; 84%), recrystallised from ethanol to give 1-(2',4'-dinitrophenyl)-5,7-dinitrobenzotriazole (15) (0.40 g) m.p. 154°. ν_{\max} : 3090, 1600, 1530, 1330 cm^{-1} .

The benzotriazole (9) (0.5 g) in sulphuric acid (96%, 10 mL) and nitric acid (100%, 10 mL) was heated under reflux for 72 h. Quenching in ice/water (200 mL) gave a pale yellow solid (0.58 g) which was recrystallised from acetone/ethanol to give 1-(2',4',6'-trinitrophenyl)-5,7-dinitrobenzotriazole (16) (0.28 g, 39%), m.p. 258° (lit. [8] 263°), ν_{\max} : 3070; 1605, 1540, 1330 cm^{-1} .

N-(2',4',6'-Trinitrophenyl)-1,2-benzenediamine (18).

Picryl chloride (2.5 g, 10.1 mmol) was added to a solution of o-phenylenediamine (1.50 g; 13.9 mmol) in methanol (50 mL), and the mixture was heated under reflux for 2 h. Cooling and filtration gave a green/yellow solid (3.1 g) which was washed with hydrochloric acid (2N, 100 mL) and recrystallised from xylene to give (18) as red crystals (1.35 g, 42%), m.p.

181°. ν_{\max} : 3420, 3360, 3280, 3100; 1610, 1590, 1530, 1510, 1335, 1320, 1295 cm^{-1} ; ^1H n.m.r.: δ 8.90 s, 2H, H_3', H_5' ; 7.20-6.20, complex multiplet, 4H, H_3-H_6 .

1-(2',4',6'-Trinitrophenyl)benzotriazole (17).

A mixture of the diamine (18) (0.5 g), acetic acid (20 mL) and sodium nitrite (0.40 g) was stirred for 2 h and then poured into water (60 mL) to give an off white solid (0.45 g). Chromatography (silica/methylene chloride) gave (17) as the major product (0.25 g, 48%) which was recrystallised from ethanol to give yellow needles, m.p. 219°. ν_{\max} : 3090; 1620, 1560, 1350 cm^{-1} ; ^1H n.m.r.: δ 9.45, s, 2H, H_3, H_5 ; 8.50-7.50, complex multiplet, 4H, H_3-H_6 .

Nitration of the diamine (18).

The diamine (18) (1.0 g) was added to a 1 : 1 mixture (20 mL) of nitric acid (100%) and sulphuric acid (96%). After the exothermic reaction cooled, the mixture was heated under reflux for 24 h and then worked up by quenching in ice/water (250 mL). The resultant pale yellow solid was recrystallised from ethanol to give (16) (0.40 g, 31%), identical with (16) prepared previously.

2-Amino-2',3,4',5,6'-pentanitrodiphenylamine (21).

3,5-Dinitro-1,2-benzenediamine (19) was prepared by reduction of 4,6-dinitrobenzofuroxan with hydroiodic acid [14], and was converted to (21) by reaction with picryl chloride in dimethylformamide [8].

1-(2',4',6'-Trinitrophenyl)-4,6-dinitrobenzotriazole (22).

Aqueous sodium nitrite (10%, 5 mL) was added dropwise with stirring to the diamine (21) (0.5 g) in sulphuric acid (96%, 25 mL) at 5° such that the temperature did not exceed 15°. After a further 1 h, the reaction mixture was poured onto ice. The resulting solid was collected and recrystallised (acetone/ethanol) to give as a yellow solid, m.p. >250° (dec) 1-(2',4',6'-trinitrophenyl)-4,6-dinitrobenzotriazole (0.23 g; 46%) (22); ν_{\max} : 3080, 1600, 1530, 1330 cm^{-1} .

2-Amino-2',4,4',5,6'-pentanitrodiphenylamine (26).

This compound was prepared by the procedure of Wilson [15] which involves nitration of 1-(2',4',6'-trinitrophenyl)benzo-1,3-diazole.

1-(2',4',6'-Trinitrophenyl)-5,6-dinitrobenzotriazole (25).

The diamine (26) (0.4 g) was suspended in acetic acid (20 mL), and sodium nitrate (0.4 g) was added with stirring over 0.5 h. The solid residue was filtered and the filtrate was poured into water (80 mL). The precipitate (0.35 g) was recrystallised from ethanol to give 1-(2',4',6'-trinitrophenyl)-

5,6-dinitrobenzotriazole (0.26 g, 63%), m.p. 260° (lit. [8] 226°) (25) as off-white crystals, ν_{\max} : 3070, 1610, 1540, 1340 cm^{-1} .

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TABLE 1

¹H NMR SPECTRA OF POLYNITROBENZOTRIAZOLES

COMPOUND	BENZOTRIAZOLE SIGNALS	OTHER SIGNALS
9	H ₄ 9.07(d); H ₆ 9.51(d) J~2Hz	9.42, 5H, s, Ph
14	H ₄ 9.12(d); H ₆ 9.67(d) J~2Hz	8.47, 2H, d, H _{3'} , 5', 8.00, 2H, d, H _{2'} , 6', J ~ 9Hz
15	H ₄ 9.20(d); H ₆ 9.76(d) J~2Hz	9.12, 1H, d, H _{3'} , 8.88, 1H, dd, H _{5'} , 8.34, 1H, d, H _{6'} , J _{3',5'} ~ 2.5 Hz J _{5',6'} ~ 9 Hz
16	H ₄ 9.25(d); H ₆ 9.84(d) J~2Hz	9.45, 2H, s, H _{3'} , 5',
22	H ₅ 9.57(d); H ₇ 9.02(d) J~2Hz	9.52, 2H, s, H _{3'} , 5',
25	H ₄ 9.51(s); H ₇ 9.11(s)	9.51, 2H, s, H _{3'} , 5',

TABLE 2

DENSITIES OF BENZOTRIAZOLES

COMPOUND	CALCULATED DENSITY (Mg/m ³)	MEASURED DENSITY (Mg/m ³)
9	1.57	1.56
14	1.67	1.62
15	1.74	1.67
16	1.81	1.74
17	1.67	1.69
22	1.81	1.78
25	1.81	1.74

TABLE 3

THERMAL CHARACTERISTICS OF BENZOTRIAZOLES

COMPOUND	mp(°C) (HOT STRIP)	DSC CHARACTERISTICS		
		TEMP	EVENT	ENERGY (kcal mole ⁻¹)
9	208	480 K (207°C)	Fusion	8.3
14	204	477K (204°C)	Fusion	6.6
		610K (337°C)	Exotherm	12.8
15	154	424K (151°C)	Fusion	6.0
		600K (327°C)	Exotherm	33.9
16	258	529K (256°C)	Fusion	9.6
		581K (308°C)	Exotherm T of I 304°C)	152.6
17	212	491K (218°C)	Fusion	7.6
		576K (243°C)	Exotherm (T of I 235°C)	102.3
22	-	585K (312°C)	Exotherm (T of I 289°C)	103.7
25	260	528K (255°C)	Fusion	10.4
		549K (276°C)	Exotherm (T of I 267°C)	142.4

TABLE 4

EXPLOSIVE PROPERTIES OF BENZOTRIAZOLES

COMPOUND	V OF D ^a (m/s)	P _{CJ} ^b (GPa)	F OF I	ELECTROSTATIC SENSITIVITY
9	4920	0.30	>200	Blackens at 4.5J
14	6040	11	150	Blackens at 4.5J
15	6810	18	120	Ignites at 4.5J, but not at 0.45J
16	7370	23	30	Ignites at 4.5J, but not at 0.45J
17	6040	11	20-40 ^c	
22	7370	23	60	
25	7370	23	40 ^c	

a Calculated Velocity of Detonation [12]

b Calculated Detonation Pressure [12]

c Limited "screening" tests only: insufficient material was available for full Rotter Impact Testing.

END

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DTIC